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Short communication

Free chlorine detection based on EC' mechanism at an electroactive polymelamine-modified electrode

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ABSTRACT

This work presents the application of an electroactive polymelamine-modified screen printed carbon electrode (polymelamine-SPCE) for free chlorine (free-Cl) detection. It is based on EC' mechanism for electrocatalytic detection of free-Cl with the azo (i.e., –N═N–) functionality of polymelamine first reduced electrochemically followed by oxidization with free-Cl in a cyclic manner. The polymelamine-SPCE showed a wide linear range from 10 μM to 7 mM ($R^2 = 0.9957$) and a detection limit of 5.5 μM (S/N = 3) for free-Cl detection by flow injection analysis in neutral media. It was successfully demonstrated for the determination of free-Cl in swimming pool and tap waters.

1. Introduction

Free-Cl (commercially available as hypochlorite in alkaline solution) is used as disinfectant and deodorizer to destroy disease-causing bacteria and extensively employed in everyday life ranging from household bleaching, disinfection of drinking water and swimming pool water, hospitals, to industries in effluent treatment [1–4]. Free-Cl concentration (the sum of dissolved chlorine gas (Cl_2), hypochlorous acid (HOCl) and hypochlorite ion (ClO^-) depending on the pH of the medium [5]) is of special importance to define levels of the quality of disinfection and thus proper control and monitor of free-Cl is necessary [6]. Its determination is normally carried out by means of the *N*,*N*-diethyl-*p*-phenylenediamine (DPD) colorimetric method [7]. Nonetheless, the DPD method cannot be applied in continuous systems. The development of autonomous analytical systems to overcome the drawback for free-Cl monitoring is therefore of high interest.

Compared to various methods employed for free-Cl determination [8–10], electroanalytical method is simple to apply in continuous monitoring. Unfortunately, the reported electrodes for the determination of free-Cl at cathodic potential are too complicated and expensive [11–14]. The reduction potential for free-Cl is also close to dissolved oxygen reduction potential that makes the detection difficult [15]. As to the anodic determination of free-Cl, deterioration of electrodes to result in fouling of the electrode remains a problem. This would then require pretreatment of the electrodes which renders the method unsuitable for continuous on-line monitoring. Boron-doped diamond (BDD) electrodes were reported to solve the problem for determining the concentration of free-Cl [16]. Yet, the use of disposable screen printed carbon electrode (SPCE) obviously can make the analytical work more convenient in real field application [17].

Recently, our group has reported the background of an electroactive polymelamine with the azo and hydrazo functionality [18]. The formation of azo functionality by hypochlorite (free-Cl) has been reported to involve in the oxidation of hydrazo (i.e., –NH–NH–) functionality with certain selectivity in fluorescent sensor [19,20]. It is interesting that this specific reaction is also true at the polymelamine-SPCE with the hydrazo functional group to selectively react with hypochlorite (free-Cl). We present here our effort in developing this disposable sensor for the determination of free-Cl in swimming pool and tap waters.

2. Materials and methods

Hypochlorite (12%) was purchased from SHOWA. Melamine was obtained from Sigma-Aldrich and all other compounds were of analytical grade and used without purification. Aqueous solutions were prepared with double distilled water. For all experiments, the SPCE (geometric area = 0.196 cm^2) obtained from Zensor R&D (Taichung, Taiwan) was preanodized by applying a potential of 2.0 V for 300 s in 0.1 M, pH 7 PBS. Electropolymerization was done by cycling between 0.2 and 1.5 V in 0.1 M HCl containing 1 mM melamine for 20 segments [18,21]. As free-Cl easily undergoes auto-decomposition, 1% free-Cl (i.e., 1% (v/v) hypochlorite) solution was freshly prepared from 12% hypochlorite solution and determined its concentration spectrophotometrically (Model U 3000, Hitachi, Japan) at 294 nm before use [22].

Electrochemical experiments were carried out with a CHI 832 electrochemical workstation (CH instruments, Austin, TX) using the polymelamine-SPCE working, Ag/AgCl reference, and platinum auxiliary

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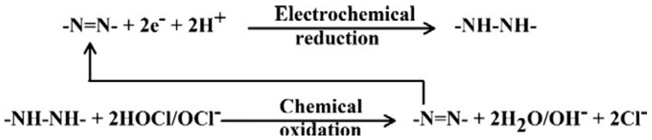
electrodes. The dynamic amperometric experiments were carried out at a FIA system as reported earlier with a 0.1 M, pH 7 PBS carrier solution [23]. The AFM images were recorded with a multimode scanning probe microscope system operated in tapping mode using Being Nano-Instruments CSPM-4000 (Ben Yuan Ltd., China). Swimming pool and tap waters were collected freshly, adjusted the pH to 7 (PBS) and subjected to detection without any pre-treatment. Results of free-Cl detected by the proposed method were compared to the DPD method [7].

3. Results and discussion

Fig. 1 shows the cyclic voltammograms of the polymelamine-SPCE in the absence/presence of free-Cl in 0.1 M, pH 7 PBS. The polymelamine-SPCE exhibits a well behaved redox reaction with an enhancement in the cathodic peak current after the addition of free-Cl. The increase in current comes from the reduction of the functional group of −N═N− to −NH−NH− and then catalytically oxidized by free-Cl in a cyclic manner. It is based on EC' mechanism, as illustrated below:



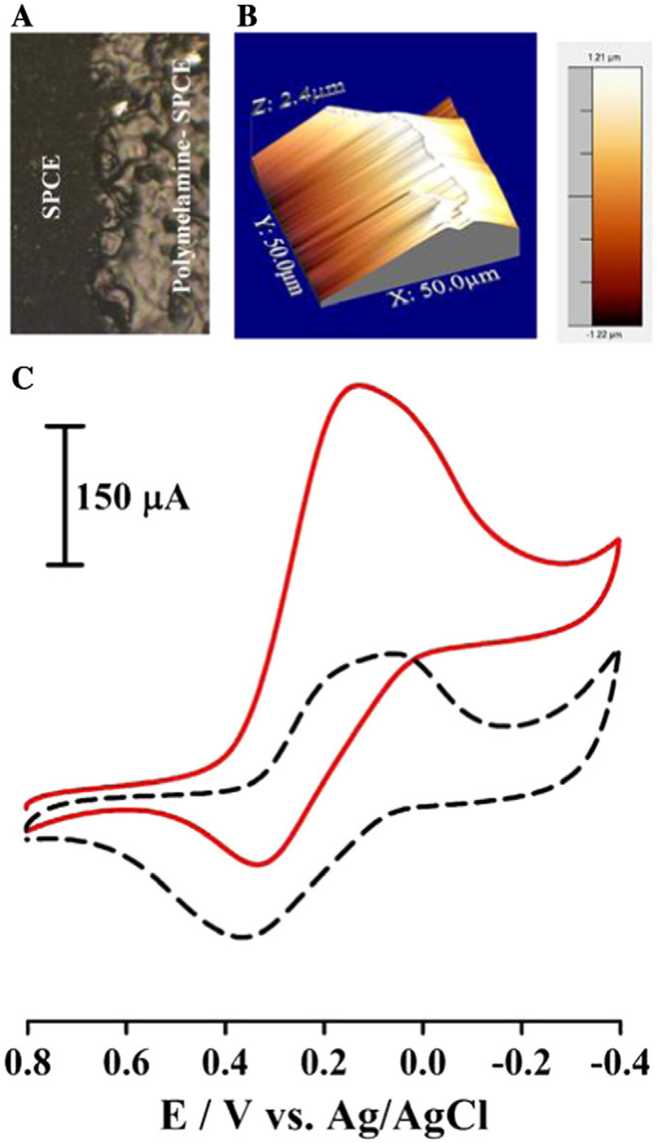


Fig. 1. (A) Optical image of SPCE and polymelamine-SPCE. (B) AFM image of (A). (C) Cyclic voltammograms observed at the polymelamine-SPCE in the absence (black dashed line)/presence (red solid line) of 7 mM free-Cl in 0.1 M, pH 7 PBS under a scan rate of 50 mV/s.

As shown in the figure, the polymelamine was characterized by AFM and a film thickness of 2.4 μm was formed on SPCE. Based on Cottrell equation [24,25], chronoamperometry was next employed to investigate the kinetic behavior of catalytic reaction at 0.125 V. To calculate diffusion coefficient (D), a plot of $Qt^{-1/2}$ vs. free-Cl (Fig. 2A inset (i)) was drawn using the data obtained from Fig. 2A. According to Eq. (1):

$$Q = \left(2nFA(Dt)^{1/2}C\right)/\left(\pi^{1/2}\right) \qquad (1)$$

the value of D can be calculated from the slope of the plot as 4.16×10^{-6} $\mathrm{cm^2\,s^{-1}}$. The catalytic reaction rate constant (k) was calculated using Eq. (2):

$$I_{cat}/I_L = (\pi kCt)^{1/2}. \qquad (2)$$

From the slope of the plot I_{cat}/I_L vs. $t^{1/2}$ (Fig. 2A inset (ii)) for 3 mM free-Cl, the value of k was determined as 2034.71 $\mathrm{M^{-1}\,s^{-1}}$. This explains the sharp feature of catalytic peak observed for reduction of free-Cl at the polymelamine film. Scan rate effect to this electrocatalytic phenomenon was further studied. As shown in Fig. 2B, the plot of log (i_{pc}) against the scan rate results in a linear plot with a slope of 0.55, suggesting that the reaction is diffusion-controlled. This favors the application of FIA in continuous monitoring of free-Cl. The hydrodynamic experimental parameters of 1.3 mL/min flow rate (Fig. 2C) and 0.125 V detection potential (Fig. 2D) were optimized and used in subsequent studies.

Fig. 3A shows the observed FIA responses for the calibration plot with a wide linear range from 10 μM to 7 mM (regression coefficient of 0.9957) and detection limit of 5.5 μM (S/N = 3) based on 7 repeated injection of 10 μM free-Cl. Note that this concentration range matches the minimum and maximum legal chlorine concentration between 1 and 3 mg/L (i.e., 19.4 and 58.3 μM) permitted by "WHO" [6]. Table 1 summarizes the advantage of the proposed method for free-Cl determination and the main advantage of our system lies in its simple application in continuous monitoring. Finally, it is concerned that the strong oxidizing properties of free-Cl might affect the polymelamine under consecutive measurements and thus the repeatability of the system under multiple injection of free-Cl was checked. As shown in Fig. 3B, with 30 continuous injections of 1 mM free-Cl, a relative standard deviation of 1.7% was obtained. These observations indicate that the polymelamine-SPCE is highly stable under continuous operation. The storage stability of electrode was checked regularly for a period of 7 days and a current response of 95% was retained on final day.

For the successful selective detection of free-Cl in real field application, the influence of coexisting species was studied. As can be seen (Fig. 3C), only free-Cl gave a signal while the other species exhibited almost no response upon injection. The excellent selectivity for free-Cl over other species shows that polymelamine-SPCE has potential applications for free-Cl detection in complex environmental samples.

In order to validate the potential applicability of the polymelamine-SPCE, the determination of free-Cl in swimming pool and tap waters was evaluated. Upon injection, swimming pool water was found to contain 20 μM of free-Cl; whereas no free-Cl was detected in tap water. The matrix effect is also negligible in real sample analysis. For swimming pool and tap waters, the recoveries were found to be in the range of 97–102%. These results approve the polymelamine-SPCE's applicability